



## SEM study of crystal morphology in the $Zn_4(OH)_6SO_4 \cdot nH_2O$ system ( $n = 1, 3, 4, 5$ )

### SEM изследване на кристална морфология в системата $Zn_4(OH)_6SO_4 \cdot nH_2O$ ( $n = 1, 3, 4, 5$ )

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#### Introduction

Minerals with the composition  $Zn_4(OH)_6SO_4 \cdot nH_2O$  are among the rare cases of reversible mutual conversion under air relative humidity changes at ordinary temperatures. The group includes minerals osakaite (with 5  $H_2O$  per formula unit), namuwite (with 4  $H_2O$ ), lahnsteinite (with 3  $H_2O$ ), as well as the monohydrate, which is not found in nature, but it is obtained from the others minerals already mentioned at extremely low humidity (Stanimirova et al., 2017). All they have a layered structure composed of decorated interrupted hydroxide sheets (Hawthorne, Schindler, 2000; Hawthorne, Sokolova, 2002) and form tabular to flaky crystals with trigonal or pseudo-trigonal triclinic symmetry. In natural conditions, they are formed as alteration products of zinc ores and slags. Also, osakaite was found in samples immediately after taking them in the mine, namuwite – in a sample stored in the National Museum of Wales, and lahnsteinite – in a sample from a museum in Germany, i.e., in samples stored in an atmosphere with different relative humidity. Bear et al. (1987) found their mutual transformations in the study of hydrometallurgy of zinc and lead, and Stanimirova et al. (2017) confirm and clarify these results and propose structural schemes of conversions. It is shown that during the transformations the lattice parameter  $a$ , which depends on the hydroxide layer, remains unchanged, while the parameter  $c$ , depending on the changes in the composition and structure of the interlayer, changes significantly – from 11.027 Å in osakaite to 7.23 Å in the monohydrate. This shift associate with a change in the edge angle between the faces of the crystals.

The question arises, do the crystals change morphologically under the conditions of the deep vacuum in the column of a scanning electron microscope (SEM) and the image of which modification we see in the photos after we have placed a mineral type determined by diffraction?

In the present work, we seek answers to these questions using a previously described method (Kirov, Dencheva, 2016) for indexing of crystal faces of micro- and nano-sized crystals.

#### Materials and methods

*Namuwite preparation and characterization.* The investigated sample was prepared by alkalization reaction of 1M  $ZnSO_4$  solution through hydrolysis of urea at 94–96 °C for 2 hours, followed by filtration, washing with distilled water, and air-drying. The phase composition of the obtained product was analyzed by powder X-ray diffractometer TuR M62 using filtered Co-radiation. The SEM investigations were carried out using a JEOL 5510 microscope.

*Indexing faces of crystals on SEM images.* SEM photos present a parallel-perspective (orthographic) projection of the object onto a plane perpendicular to the electron beam. The projections of crystals drawn on goniometric or structural data are also orthographic, which allows the comparison of SEM-photograph of a crystal with model images of the studied phase. To achieve such a comparison, it is necessary to obtain an adequate model image of the crystal and to compare this model with the real image, keeping in mind that the orientation of the crystals in the sample is accidental.

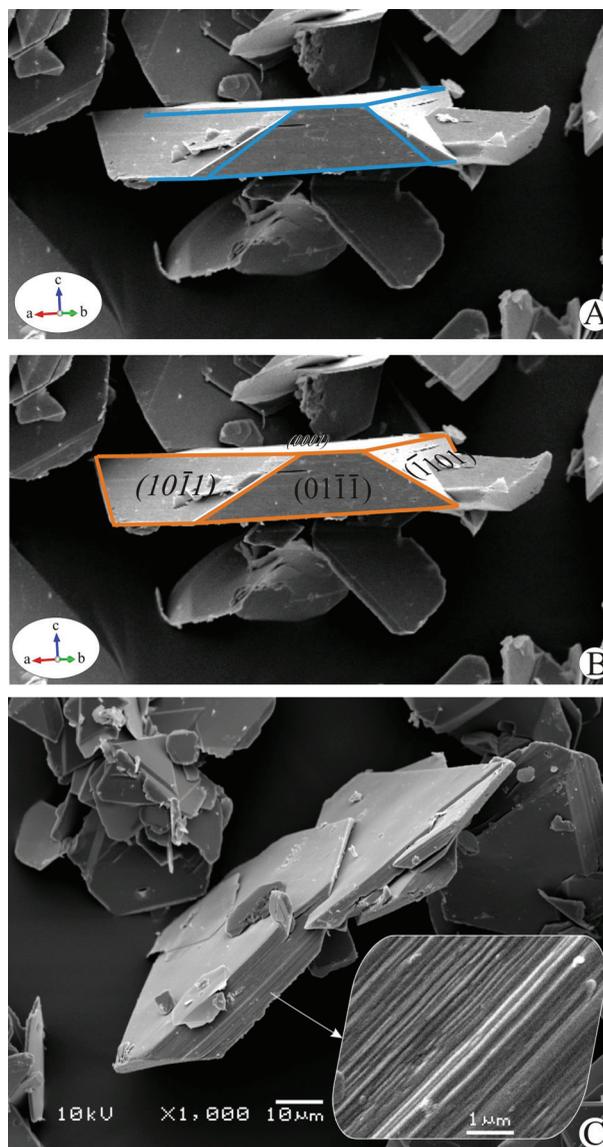
*Morphological simulations* are based on the Bravais-Friedel-Donnay-Harker (BFDH) law and on the theory of PBC (periodic bond-chains) vectors. Model images of the crystals were obtained using the computer program VESTA (Momma, Izumi, 2011) after the introduction of lattice parameters, space group, and indexes of the expected morphologically important forms following BFDH-law and the method of PBC-vectors.

## Results

*Sample.* PXRD analysis of the obtained product revealed namuwite as a single crystal phase in the studied sample. SEM images of typical namuwite crystals are shown in Figure 1.

*Indexation of namuwite crystals.* Examination of the SEM images shows that the basic pinacoid and rhombohedron are the only represented forms in the namuwite crystals. According to the namuwite powder XRD data, the basal-pinacoidal 0001 and rhombohedral planes  $10\bar{1}1$  have largest d-spacing value: 10.50 Å and 5.91 Å, respectively. The analysis of possible PBC vectors in the structure shows that in the pinacoidal plane lie three intersecting systems of vectors, and in the rhombohedron – one vector and therefore these forms are most probable in the studied sample as F- and S-forms, respectively (Hartman, Perdok, 1955). Based on these predictions, model images of possible crystal forms of  $\text{Zn}_4(\text{OH})_6\text{SO}_4 \cdot n\text{H}_2\text{O}$  with different degrees of hydration and different combinations of basic pinacoid and rhombohedron were constructed. Using program Alpha V or Ghost the graphic (linear) variant of the image of the real crystal leaves is on the screen as a foreground. This allows the projection of simulated crystal forms under it. Then, using the capabilities of the VESTA program, various crystal shapes are generated until the morphology of the real object and the simulated one are completely matched.

The results obtained following this procedure, show that the constructed model image of a namuwite crystal with  $a = 8.33$  and  $c = 10.54$  Å does not fit the microscopic image of a real crystal (Fig. 1A). The same result is obtained for the model image constructed using the lahnsteinite parameters ( $c = 9.30$  Å). The attempts to fit the real image with crystal models constructed from the rhombohedra with other indexes (as  $\{10\bar{1}2\}$ ,  $\{20\bar{2}3\}$  etc.) were also unsuccessful. A good fit was achieved only by using the crystal model based on the monohydrate parameter  $c = 7.22$  Å (Fig. 1B). In this case, all the edges of the model image are parallel to the analogous edges in the SEM image of the real crystal regardless of its orientation in the sample.



**Fig. 1.** Micrographs of namuwite crystals in SEM: *A*, unsuccessful fit with a model image based on namuwite parameters; *B*, successful fit with a model image based on monohydrate parameters; *C*, morphology of the face  $(10\bar{1}1)$  (in the inset photograph)

## Discussion

The data from the morphological study unambiguously shows that the namuwite has become a monohydrate phase for a very short time of the experiment in the column of the microscope (at a pressure of  $10^{-6}$  torr). The namuwite-lahnsteinite-monohydrate transition accomplishes over dehydrated zeolite at room temperature for more than 24 hours and at 130 °C in the air (Stanimirova et al., 2017). In this transition, the two layers of interlayer water molecules are removed from the structure and only those taking apical positions in  $\text{Zn}(\text{OH})_3\text{H}_2\text{O}$  tetrahedra

remain. This leads to insignificant changes in the lattice parameters  $a$  and  $b$  and reduction of the symmetry to triclinic ( $P\bar{1}$ ), but the crystals retain their rhombohedral character. However, the edge angles between the crystal faces change significantly. Thus, the angle  $(001)^\wedge(101)$  changes from  $55.61^\circ$  in the namuwite to  $45.02^\circ$  in the monohydrate. Interestingly, the change in the slope and width of the rhombohedral face does not affect its integrity and its flat character. Its surface is streaked with layers 60–70 to 200 nm thick (Fig. 1C), which are probably packages of hydroxide layers slipped during the solid-state structural transformation caused by dehydration.

## Conclusion

For the first time, a change in the morphology of crystals associated with reversible dehydration processes was revealed and discussed. It was found that in the column of the scanning electron microscope the dehydration proceeds at a high rate and reaches the maximum possible degree that can be achieved

at room temperature. The microscopic images show the shapes of the transformed monohydrate phase.

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